

# MODELING OF BATCH MICROEMULSION COPOLYMERIZATION OF VINYL ACETATE/BUTYL ACRYLATE

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## Abstract

A mathematical model, with a minimum of adjustable parameters and taking into account the partition of monomers between the different phases during polymerization, was developed and applied to simulate the kinetics, particle size, particle number and copolymer composition of the vinyl acetate/butyl acrylate monomer mixture in microemulsion media, in batch reactions. A correlation for the radical desorption coefficient, as a function of the rate of monomer chain transfer and the probability of desorption of a single unit radical, were used. The radical capture by micelles and particles was assumed to be reversible and to occur by diffusion. The model takes into account both micellar and homogeneous nucleation. Results of the simulations show that the average number of radicals per particle was less than 0.5 and it was attributed to the fast exit of radicals generated by chain transfer to monomer. Good agreement between the model and the experimental results was observed.

## Introduction

Microemulsion polymerization is a complex heterogeneous process where transport of monomers, free radicals and other species (such as chain transfer agent, co-surfactant and inhibitors) between the aqueous and organic phases, take place. Compared with other heterogeneous polymerization processes (suspension or emulsion) microemulsion polymerization is a more complicated system. Polymerization rate is controlled by monomer partitioning between the phases, particle nucleation, and adsorption and desorption of radicals [1].

The kinetics of microemulsion polymerization have much in common with emulsion polymerization kinetics, the most characteristic feature of which is the compartmentalization, where the radicals growing inside the particles are separated from each other, thus suppressing termination to a high extent and, as a consequence, providing high rates of polymerization. Only few works have been devoted to model kinetics of microemulsion polymerization. Guo *et al.* [2,3] developed a model for polymerization of styrene in microemulsion media with four components. They considered that nucleation occurs in the microemulsion droplets and when these disappear, nucleation can be continued by entry of a radical from the water phase to the so called *mixed micelles* formed with surfactant, co-surfactant and a small amount of monomer. This model is able to predict the experimental data only at low conversions. Morgan *et al.* [4] have discussed in detail a theoretical model for the conversion and rate of polymerization of hexyl methacrylate. They assumed that the constants for capture of radicals by particles and micelles have the same value. Moreover, they suppose that all the radicals generated within particles by chain transfer to monomer are desorbed and the radicals remain active during all the reaction. This model predicts very well the experimental conversion and reaction rate data for the microemulsion polymerization of hexyl methacrylate, nevertheless, it does not predict the density in number of particles, or the size of particles and the molecular weight of the polymer. In addition, it predicts that the maximum polymerization rate always occurs at the

same conversion value, independently of the monomer used, which is in opposition to what has been experimentally observed [5,6].

Mendizábal *et al.* [7] presented a model that describes conversion, average molecular weight, average particle size, and average number of polymer chains per particle as a function of time. In this model micellar and homogeneous nucleation are taken into account because the great amount of surfactant present in microemulsion polymerization makes possible the stabilization of precipitated oligomers through the reaction. This model predicts experimental data for the microemulsion polymerization of monomers with different water solubility but requires the estimation of parameters such as the propagation rate constants in the water phase as well as the constants of radicals capture by micelles and particles.

Sanghvi *et al.* [8] used a mathematical method to represent the kinetics data of the microemulsion copolymerization of styrene/acrylonitrile system. This model does not use monomer partition calculations between each phase, it uses an overall monomer concentration and has one adjustable parameter. The model proposed by Sanghvi deviates significantly from the experimental data at high conversions.

The purpose of this work is to model the batch microemulsion copolymerization. Another goal of this research is to test the model with the VAc/BuA system using a mixture of SDS/Brij-35 as emulsifier to provide the required data for a future comparative study with semibatch microemulsion copolymerization. Because the majority of the semibatch emulsion and microemulsion polymerization processes start up with low monomer concentrations, the kinetic behavior of the system was the main focus of this study.

## Theory

The mathematical model used to simulate the experimental data here obtained has been reported by us in a previous work [9]. The main feature of the model includes micellar and homogeneous nucleation and thermodynamic equilibrium for the calculation of monomer partitioning between the phases. In this work, the model has been modified and instead of using adjustable parameters, correlations have been used to calculate kinetics and transport parameters as described next.

### *Radical capture by micelles and particles.*

Radical capture was assumed to occur by diffusion of the active species to the reaction sites. The rate coefficient for radical capture by micelles and particles is given by [10]:

$$k_{cmi} = 4\pi r_m F_j D_{wi} N_{Av}$$

$$k_{cpi} = 4\pi r_p F_j D_{wi} N_{Av}$$

where  $k_{cmi}$  and  $k_{cpi}$  are rate coefficient for radical capture type  $i$  by micelles and particles, respectively.  $F_j$  is the radical capture efficiency,  $r_p$  and  $r_m$  the polymer particle and micelles radius, respectively, and  $D_w$  the diffusion coefficient of the radicals in the aqueous phase,  $N_{AV}$  is Avogadro's number.  $F_j$  was the only adjustable parameter and accounts for all resistances to radical entry other than diffusion [11]. The value used in the simulations for  $F_j$  was  $1 \times 10^{-5}$ .

### *Radical desorption from particles*

Individual desorption coefficients were calculated as the rate of monomer chain transfer and the probability of desorption of a single unit free radical [10]:

$$k_{di} = \frac{(k_{imAi}P_A^p + k_{imBi}P_B^p)M_{ip}(2D_p/r_p^2)}{(2D_p/r_p^2 + k_{piA}M_{Ap} + k_{piB}M_{Bp})}$$

where  $k_{imij}$  are monomer chain transfer,  $D_p$  is the diffusion coefficient of radicals in polymer particles,  $M_{ip}$  are the concentrations of monomer A and B in the polymer particles, respectively and  $P_A^p$  and  $P_B^p$  are the time averaged probability of finding a free radical with ultimate unit of type A and B, respectively, in the polymer particle phase [12] and is given by:

$$P_A^p = \frac{k_{pBA}M_{Ap}}{k_{pBA}M_{Ap} + k_{pAB}M_{Bp}}$$

and  $P_B = 1 - P_A$ .

## Results and discussions

Figure 1 shows a comparison between the experimental conversion versus time values and those predicted by the model at different monomer concentrations. Good agreement between experimental and predicted values was obtained. Polymerization rate increases as monomers concentrations increase which is well represented by the model. In Figure 2 the particle size as a function of conversion is shown, and it is observed that the model reproduces the experimental data satisfactorily. The model assumes micellar and homogeneous nucleation, and it was found that the homogeneous nucleation mechanism dominates particle formation. Homogeneous nucleation implies radical propagation in the aqueous phase until a critical size is reached in which the oligoradical precipitates. This radical can absorb free surfactant stabilizing and generating a new polymer particle. The model is useful to elucidate this nucleation mechanism predicting the particle number throughout the reaction as can be observed in Figure 3. As a matter of fact, the model predicts that non-initiated microemulsion droplets are depleted at low conversions (< 10%) indicating the end of micellar nucleation. Detailed discussions will be given in the presentation.

## Conclusions

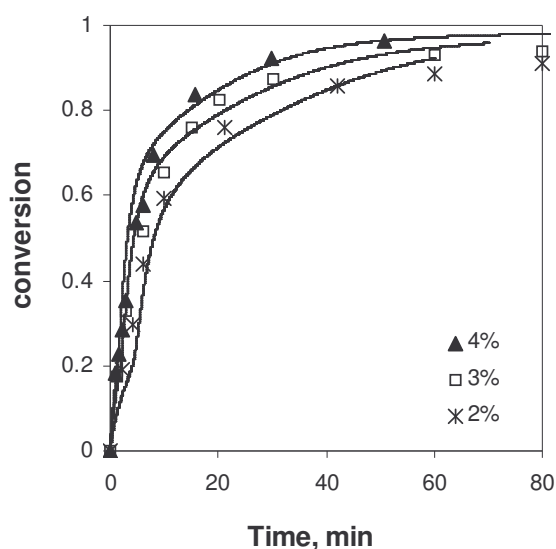
The mathematical model proposed here with a minimum of adjustable parameters satisfactorily predicts the VAc/BuA conversion vs. time data, although there are slight deviations at high conversions. Further, the model also gives a good prediction of particle diameter and evolution of number of particles throughout the reaction.

## References

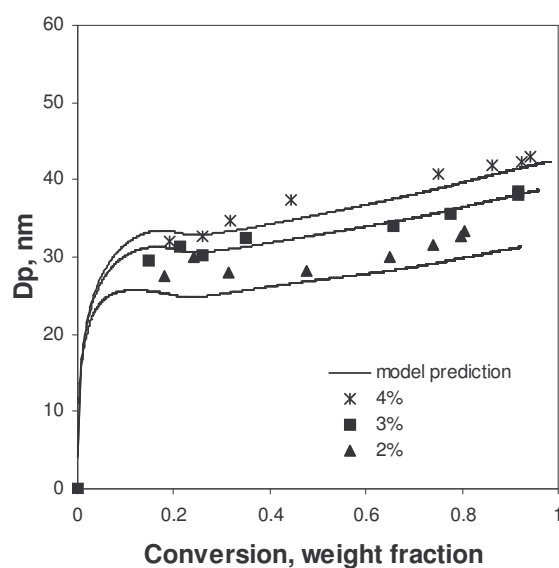
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**Figure 1.** Conversion versus time of batch microemulsion copolymerization at 60°C with 2% (w/w) of KPS respect to the monomer content at different monomer concentrations of mixture VAc:BuA (85:15 w/w) in the initial charge.



**Figure 2.** Particles size vs. conversion of microemulsion copolymerization at different monomer concentrations. Dots are experimental data and continuous curve are model predictions.

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